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## Characterization of pore water, ion transport and water-rock interaction in claystone by advective displacement experiments

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### Abstract

Displacement of preserved pore water from claystones by imposing a hydraulic gradient with an artificial pore water yields early extracts characteristic of the pore water. Long-term tracer breakthrough behavior provides transport properties and anion-accessible porosity, whereas elution of major components are controlled by ion exchange and mineral solubility. A single long-term experiment provides a comprehensive system understanding.

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**Keywords:** pore water; claystones; ion transport; water-rock interaction.

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### 1. Introduction

Pore water characterization, ionic transport and water-rock interaction in argillaceous rocks is of interest for performance assessment of deep disposal of radioactive waste and understanding processes in cap rocks (oil/gas exploitation, carbon dioxide sequestration). Direct pore water sampling is difficult<sup>1</sup>, and destructive methods such as aqueous leaching and pore water squeezing are prone to artefacts<sup>1,2</sup>. Pore water composition is reconstructed by thermodynamic modelling integrating multiple sources of data<sup>3</sup>. Transport properties are derived from dedicated experiments.

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These authors<sup>4</sup> presented first results from a new method called “advective displacement” whereby a confined core sample was subjected to a hydraulic gradient inducing a flux for sampling small aliquots of displaced pore water. Early extracts closely resemble the in situ composition, and the recorded breakthrough of select injected tracers (anions,  $^2\text{H}$ ) provides transport properties. A single long-term experiment can thus yield a comprehensive pore water characterization and system understanding. This paper details the technique and its limitations with results from clayey lithologies from a Mesozoic sequence underlying the Swiss Molasse basin (deep boreholes) or accessible in the Swiss Jura Mountains (Mont Terri underground rock laboratory).

## 2. Advective displacement method, sample preparation and analysis

Core samples (70-100 mm diameter), preserved and protected on site, are cut (50-100 mm length) and placed between thin filter discs (Teflon supported by porous titanium) and titanium coupling pieces (Fig. 1). Chemical and hydraulic isolation from the confining fluid is achieved by inner Teflon layers and an outer latex sleeve. The resultant core assembly is placed into a triax-type apparatus, imposing a fixed core length with an adjustable spindle, and subjected to a water confining pressure (5-10 MPa). Chosen infiltration pressures of 3-8 MPa impose hydraulic gradients of  $3\text{-}16 \cdot 10^3$  m/m, and this induces volumetric flow rates of 0.2-1 ml/week. Confining pressure is maintained by an equivalent argon pressure, and infiltration is driven from a polymer-coated steel cylinder pressurized by helium.

Parameters measured in-line include electric conductivity (Fig. 1), and intermittently pH (and Eh) with small-volume ( $\sim 20$   $\mu\text{l}$ ) flow-through cells. Sampling of aliquots is done in syringes, 0.5-1 ml for early aliquots. Ideally, 1-2 pore volumes are pushed through a core (5-25 months) for providing transport properties and a concise data set for reactive transport modelling interpretation. Analytical methods include IC, ICP-OES, titration, photometry, DIC/DOC, and CRDS for stable water isotopes. Hydraulic conductivity is calculated from volumetric flow rates evaluated at each sampling time, hydraulic gradient and sample dimensions. Initial and post-mortem analysis of core material includes physical properties, mineralogy, aqueous extracts and cation occupancy and exchange capacity.

Artificial pore water composition ( $\text{Na-Cl-SO}_4\text{-Ca-Mg-K}$ ) is thermodynamically modelled to approximately match the expected salinity of the in situ pore water (4-10 g/l Cl) and constrained by selected mineral saturation. Tracers added include deuterated water and different combinations of anions ( $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ) at concentrations of 40-120 mg/l.

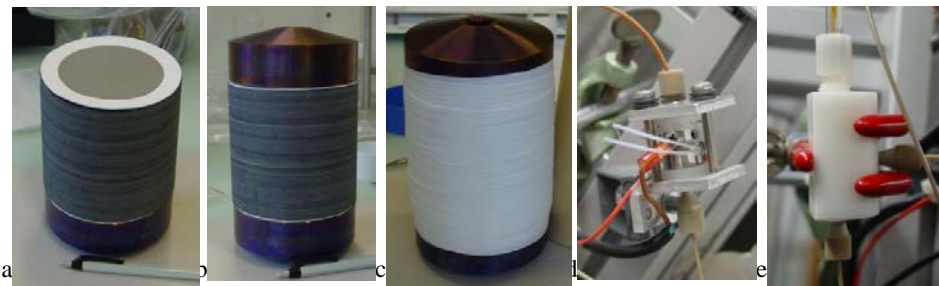


Fig. 1. (a-c) sample preparation (see text), (d) electric conductivity, (e) pH cell. Diameter of capillary tube is 1.6 mm.

## 3. Results

### 3.1. Sample characteristics, hydraulic and transport properties

Samples from three different formations with physical properties determined at the end of an advective displacement experiment (Tab. 1) possess water-loss porosities of 5.6-16.5 vol% and hydraulic conductivities of  $4\text{-}40 \cdot 10^{-14}$  m/s. Rocks are argillites to calcareous marl, all containing a portion of illite/smectite mixed layers.

A characteristic feature of claystone is its osmotic character resulting from negatively charged clay mineral surfaces that restrict anions to a smaller porosity domain compared to water and cations. This leads to an increased average linear velocity for anions under an advective regime, with distinctly faster breakthrough times relative to

water. Breakthrough curves for tracers ore pore water components (Fig. 2) are plotted against time converted to pore volume fractions (based on the measured total water content). Anions tend to reach full breakthrough concentration already after 1 pore volume, whereas breakthrough of deuterium is distinctly delayed. Even a small difference in transport between Cl and Br can be resolved (Fig. 2b), whereas SO<sub>4</sub> behaves as a reactive component. In this latter example, initial Br is flushed out and a significant initial difference in chloride concentration is evened out.

Table 1. Select properties of samples and experiments.

#	Formation	Sample ID	Clay cont.	Water cont.	WL-porosity	Diameter	Length	PW mass	K	Duration	Tracers
	name	label/depth(m)	wt% clay (I/S)	wt%	vol%	mm	mm	g	10 <sup>-14</sup> m/s	d	
1	Opalinus Clay	BPC-A1 (10 m)	70 (15)	6.80	16.5	79	120	97.1	21	5110+	<sup>2</sup> H, Br
2	Effingen Member	GOS-122.89	20 (6)	2.14	5.62	96.5	111	45.6	13	430	<sup>2</sup> H
3	Opalinus Clay	SLA-938.57-AD	83 (6)	4.80	12.2	101	101	99.2	35	817	<sup>2</sup> H, I, NO <sub>3</sub>
4	Brown Dogger	SLA-779-78-AD	64 (15?)	5.03	12.7	101	96.4	98.9	3.9	635	<sup>2</sup> H
5	Brown Dogger	SLA-811.95-AD	66 (4)	5.30	13.4	101	84.6	91.0	40	687	<sup>2</sup> H, I, NO <sub>3</sub>

1: Mont Terri URL, 2: Gösigen borehole, 3-5: Schlattingen borehole; I/S=illite/smectite mixed layers; WL=water loss (105°C)

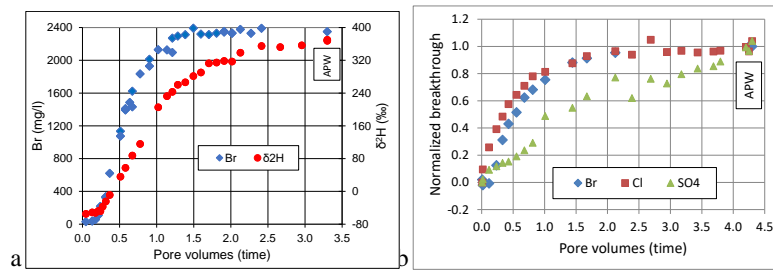


Fig. 2. (a) #1 in Tab. 1: Br and <sup>2</sup>H (V-SMOW) breakthrough; (b) #2 in Tab. 1: Br breakout, Cl and SO<sub>4</sub> breakthrough. APW=artificial pore water

### 3.2. Geochemical evolution of effluent – ion exchange and solubility controls

Evolution of concentrations in fluid aliquots show passive behavior for breakthrough of anionic tracers (Fig. 2), and breakout of anions present in situ (Br<sup>-</sup>, I<sup>-</sup>), including chloride. Sulfate (Fig. 3) does not behave conservatively, suggesting a solubility control. This is supported by calculated saturation indices that are nearly constant for gypsum (distinctly undersaturated) and celestite (near saturation). Cations are controlled by ion-exchange processes that lead to eluted concentrations that are different from the injected pore water for the entire duration of an experiment (Fig. 3a), due to a large exchange capacity compared to the dissolved inventory. A special feature are elevated initial concentrations of mostly acetate (Fig. 3b) that are subsequently flushed out but remain at measurable levels for lactate, acetate and formate (>10 mg/l).

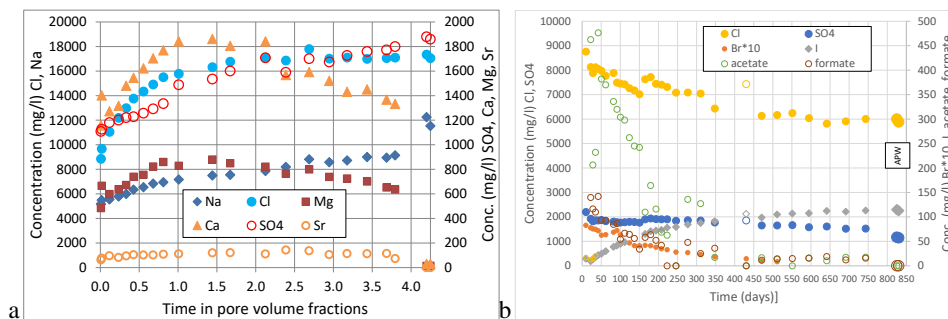


Fig. 3. (a) #2 in Tab. 1, major components; (b) #3 in Tab. 1, major components. APW=artificial pore water injected.

### 3.3. Early aliquots – composition of in-situ pore water

Early aliquots resemble in-situ pore water composition, although potentially affected by certain artefacts (see discussion). Characteristic concentrations and other parameters (Tab. 2) show salinities distinctly smaller than seawater. From this data, saturation indices and the CO<sub>2</sub> partial pressure can be calculated, assuming calcite saturation. A chloride-accessible porosity fraction ( $n(\text{Cl})/n(\text{WL})$ ) is calculated from the early chloride concentration and that measured in aqueous extracts and up-scaled to the water content. This can be done also for the last measured chloride concentration combined with post-mortem aqueous extracts of a slab from the outflow end of a core sample. There is no systematic dependency of anion-accessible porosity on clay or smectite content or salinity (Tab. 1, 2).

Table 2. Summary of early samples as proxy for pore water composition.

#	Cl	Cl_AqEx	SO <sub>4</sub>	I	Br	Na	K	Ca	Mg	Sr	del-2H	pH	P(CO <sub>2</sub> )	Cl(AqEx)/Cl
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	‰		log(bar)	n(Cl)/n(WL)
1	9000		1415		29	5410	67	580	361	35	-52	7.5	-2.6	0.6*
2	8867		1109		35	5181	104	1158	485	63		7.2	-2.6	0.33**
3	8440	3457	2070	12	8	5650	45	911	207	30	-50.6	7.2		0.41
4	3680		1298		4.1	3094	42	278	90	21	-54	7.65	-2.9	0.55**
5	6465	3409	1384	4.7	7.4	4493	59	658	180	34	-52			0.53

Cl\_AqEx: aqueous extract scaled to pore water; \* from modelling Br and  $\delta^2\text{H}$  breakthrough; \*\* from post mortem aqueous extracts

## 4. Conclusions

A single long-term experiment may provide a nearly complete description of a claystone-pore water system and some of its geochemical behavior, but artefacts are also observed. These are related to issues of small sample size and sample storage that lead to somewhat “noisy” data in the early extracts. On occasion preferential loss of water from syringes is observed that leads to an increase in dissolved salts, but not to aberrant  $\delta^2\text{H}$  compositions. This method initially releases low-molecular weight organic acids at significant concentrations (500-1500 mg/l) in contrast to aqueous extraction where such acid concentrations are closer to levels of organic acids eluted at later times. In one case indication of microbial activity was observed, namely nitrate added as anionic tracer got nearly completely reduced to ammonium, nitrogen gas and possibly nitrite (#5, Tab. 1) accompanied by CO<sub>2</sub> production. Otherwise, there was no indication of significant sulfate reduction (by organic carbon). The experimental setup is robust, but sample analysis required significant optimization of analytical methods to very small sample size. The efforts are compensated by comprehensive data sets that are also amenable to multi-component reactive transport modelling.

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